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<p>(54) Title: (CO)POLYMER MODIFICATION EMPLOYING UNSATURATED t-ALKYL PEROXYALKENYL CARBONATES</p> <p>(57) Abstract</p> <p>(Co)polymers are modified by contacting them with one or more tertiary alkyl peroxy alkenyl carbonates and decomposing the peroxide. By this process the physical properties of the (co)polymers, such as adhesion to polar substrates and lap shear strength, can be enhanced. According to a preferred embodiment, the modification reaction is carried out in the presence of a coagent whereby the advantageous polymer properties, such as adhesion to polar materials, are further enhanced. Also disclosed are shaped objects manufactured using the modified (co)polymers prepared by the process of the present invention.</p>			

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(Co)polymer Modification Employing Unsaturated t-Alkyl Peroxyalkenyl Carbonates

The invention relates to compounds useful in modifying (co)polymers, a process for modifying (co)polymers with these compounds, and to shaped objects comprising the modified (co)polymers.

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It is generally known that the introduction of epoxide or other functional groups into the appropriate (co)polymers may lead to improved physical and chemical properties of the (co)polymers. According to Rubber World 191(6), pp. 15-20 (1985) and Rubber Developments, Vol. 38, No. 2, pp. 48-50 (1985), for instance, the introduction of epoxide groups into natural rubber leads to advantages such as an increased glass transition temperature, increased oil resistance, reduced gas permeability, improved resilience, increased tensile strength and improved adhesion to other materials, such as silica fillers, glass fibers and other polymers such as PVC. Further, the polymers thus modified can be subjected to chemical reactions that are typical of epoxy groups. As examples thereof may be mentioned: i) cross-linking the polymer with polyfunctional compounds containing active hydrogen atoms, such as polyamines and dibasic acids, which is described in Chemical Reactions of Polymers, E.M. Fettes (ed.), Interscience Publications, New York (1964), chapter II, part E, pp. 152 et. seq., ii) covalently bonding antioxidants having amino groups to the polymer, which is described in Journal of Polymer Science, Polymer Letters Edition, Vol. 22, pp. 327-334 (1984) and iii) reacting the polymer with fluorine-containing compounds, such as trifluoroacetic acid, resulting in a polymer with improved lubricity and ozone resistance, which is described in WO 85/03477.

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Generally, epoxide groups are introduced into (co)polymers by so-called epoxidation reactions, in which an unsaturated (co)polymer in the form of a latex or dissolved in an organic solvent, is brought into contact with an epoxidizing reagent suitable for reacting with unsaturation present in the (co)polymer. An example of such compounds are the lower aliphatic carboxylic acids. This method, however,

suffers from several disadvantages. First, the requirement that the (co)polymer be unsaturated significantly limits the number of (co)polymers that can be epoxidized by this method. For example, saturated polymers such as polypropylene cannot be functionalized 5 using this method.

Secondly, the use of solvents in the epoxidation reaction necessitates a subsequent purification step for residual solvent removal. Such a purification step is disadvantageous from a polymer processing 10 standpoint since it adds an additional, costly processing step. Further, disposal of solvents is becoming an increasing concern because of the environmental hazards these solvents create.

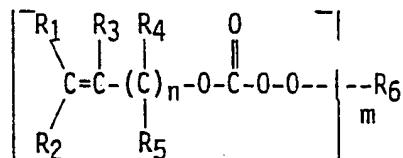
Thirdly, this type of epoxidation reaction is always accompanied by 15 undesirable side reactions, such as the formation of hydroxyl groups, acyloxy groups, ether groups, keto groups and aldehyde groups. These side reactions cause numerous problems when such epoxidation reactions are employed.

20 It is also known to prepare epoxide group-containing (co)polymers by copolymerization and graft copolymerization reactions with monomers containing a glycidyl group (cf. Journal of Polymer Science, Vol. 61, pp. 185-194 (1962), Makromol. Chem., Rapid Commun. 7, pp. 143-148 (1986) and Die Angewandte Makromolekulare Chemie 48, pp. 135-143 25 (1975)). The inevitable accompanying formation of undesirable side products, such as the formation of homopolymers of the glycidyl group-containing monomer, is a significant drawback to the practice of this method. Moreover, this method only permits preparation of a limited group of modified (co)polymers.

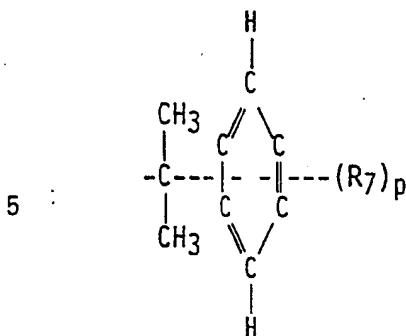
30 Bull. Soc. Chim. France No. 2, 198-202 (1985) discloses t-butyl allyl peroxide and its use for epoxypropanating organic solvents with labile hydrogen atoms. As solvents are mentioned cyclohexane, tetrahydrofuran, propionic acid, propionic anhydride, methyl propionate, acetonitrile and chloroform.

European Patent Application 0 273 990 (Akzo) discloses the use of certain unsaturated organic peroxides in the preparation of epoxide groups-containing (co)polymers. These compounds have been shown to be effective in introducing epoxide groups onto (co)polymers. However, this patent application does not disclose the compounds of the present invention. More particularly, the peroxides of the present invention are significantly different than thos of European Patent Application 0 273 990 since they contain a carbonate group between the peroxy group and the unsaturation. This is important since the present compounds are incapable of rearranging in the same manner as shown in the European Patent Application 0 273 990 and since the unsaturated free radicals generated by the present peroxy carbonates will contain a carbonate group therein.

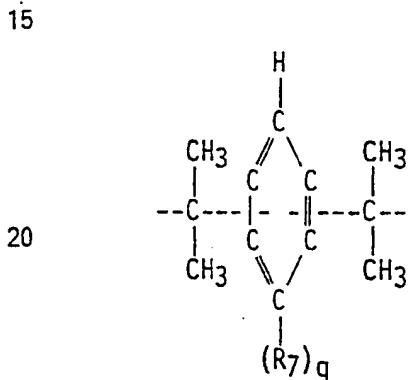
For these purposes, the present invention provides a process for modification of (co)polymers employing particular organic peroxides of the following formula:



30 wherein  $R_1$ ,  $R_2$ ,  $R_4$ , and  $R_5$  may be the same or different and represent H or  $C_{1-4}$  alkyl groups;  $n = 0$  or 1;  $m = 1$ , 2, or 3;  $R_3 = H$ ,  $C_{1-4}$  alkyl or an electron withdrawing group; and when  $m=1$ ,  $R_6 =$  a tertiary alkyl group optionally substituted with a hydroxyl group and containing 4-18 carbon atoms, p-menth-8-yl or a group of the general formula:



wherein  $p = 0, 1$  or  $2$  and  $R_7$  is an isopropenyl group, a 10 2-hydroxyisopropyl group, or an isopropyl group; when  $m = 2$ ,  $R_6$  = an alkylene group having 8-12 carbon atoms and a tertiary structure at both ends thereof, an alkynylene group having 8-12 carbon atoms and a tertiary structure at both ends thereof, or a group of the general formula:



wherein  $q = 0$  or  $1$  and  $R_7$  has the above-indicated meaning; and when 25  $m = 3$ ,  $R_6 = 1,2,4\text{-triisopropylbenzene-}\alpha,\alpha',\alpha''\text{-triyl}$  or  $1,3,5\text{-triisopropylbenzene-}\alpha,\alpha',\alpha''\text{-triyl}$ .

The alkyl, alkenyl and alkylene groups may be linear or branched, unless otherwise indicated.

30 The present invention also relates to articles of manufacture comprising one or more (co)polymers modified by the process of the present invention. More particularly, the (co)polymers modified by the process of the present are excellently suited for the manufacture of shaped objects.

Some of the compounds of the formula (I) are known in the prior art. For example, for formula (I) when n=0, species of these compounds are disclosed in Japanese Patent Application J5 9036-105-A and "A Convenient One-Step Synthesis of 1,4-Diketones," Synthetic Communications, 13(5), 361-366 (1983). These publications also disclose methods of preparing peroxy carbonates useful in the process of the present invention. To the extent that these preparation methods are disclosed, the disclosures of these publications are hereby incorporated by reference. However, these publications disclose the process of the present invention.

Compounds of the formula (I) when n=1 are disclosed in German patent application numbers DT 27 286 008 and DE 3420-048-A, British patent application GB 2081-282 and Japanese patent application numbers J6 1002-711-A, J6 1002-753-A, J5 4076-691, J5 5009-636, J6 1157-551-A and J5 4047-790. All of these published patent applications relate to the use of these unsaturated peroxy carbonates to form copolymers with various unconjugated or other monomers. These publications also disclose methods of preparing peroxy carbonates useful in the process of the present invention. To the extent that these preparation methods are disclosed, the disclosures of these publications are hereby incorporated by reference. None of these publications discloses the process of the present invention.

Finally, the use of unsaturated peroxy carbonates as polymerization initiators and as curing catalysts is disclosed in Canadian patent number 1,025,467 and U.S. patent number 4,136,105. Again, the process of the present invention is not disclosed in these publications.

Generally, the synthetic routes for making the tertiary alkyl peroxy alkenyl carbonates used in the process of the present invention are known in the art. The preferred mode of synthesizing these compounds is to react the appropriate tertiary alkyl hydroperoxide with an unsaturated chloroformate, separate the organic layer and subsequently

wash this material to provide the desired product in relatively pure form.

Suitable tertiary alkyl hydroperoxides use in this synthesis process  
5 include t-butyl hydroperoxide, t-pentyl hydroperoxide,  
t-octyl-2-hydroperoxide, and t-hexyl hydroperoxide, among others.  
Suitable unsaturated chloroformates include allyl chloroformate,  
2-propenyl chloroformate, isopropenyl chloroformate,  
2-methyl-2-propenyl chloroformate, 3-methyl-2-butenyl chloroformate,  
10 3-butenyl-2-chloroformate, 2-propenyl-2-chloroformate, and 2-butenyl  
chloroformate among others.

Typical examples of tertiary alkyl peroxy alkenylcarbonates according  
to the invention include t-butylperoxy allylcarbonate, t-pentylperoxy  
15 allylcarbonate, t-butylperoxy isopropenylcarbonate, t-pentylperoxy  
allylcarbonate, 2,5,-bis(peroxyallylcarbonate) 2,5-dimethyl hexane, t-  
nonylperoxy 2-methyl-2-pentene carbonate, t-butylperoxy-2-propenyl  
carbonate, t-butylperoxy-2-methyl-2-propene carbonate,  
t-butylperoxy-2-butene carbonate, t-pentylperoxy-2-propene carbonate,  
20 t-pentylperoxy-2-butene carbonate, t-hexyl peroxy-1,1-dimethyl2propene  
carbonate, t-butylperoxy-4-methyl-2-butene carbonate di-t-butyl  
peroxy-2-propene dicarbonate, and t-octyl peroxy 2-propene carbonate.

The peroxides can be prepared, transported, stored and applied as such  
25 or in the form of powders, granules, solutions, aqueous suspensions,  
emulsions or pastes. Other forms may also be useful in specific  
circumstances.

Which of these forms is to be preferred partly depends on the ease of  
30 feeding the peroxide into closed systems. Also, considerations of  
safety may play a role to the extent that desensitizing agents may  
have to be incorporated in certain compositions to ensure their  
safety. As examples of suitable desensitizing agents may be mentioned  
solid carrier materials such as silica, chalk and clay, inert  
plasticizers or solvents such as mono- or dichlorobenzene, and water.

1 The present t-alkylperoxy alkenylcarbonates are exceptionally well  
2 suited for use in the preparation of epoxide, cyclic carbonate and/or  
3 ketone groups-containing (co)polymers, in which process a non-modified  
4 (co)polymer is brought into contact with the t-alkylperoxy  
5 alkenylcarbonate in order to cause modification of the (co)polymer.

6 The peroxy alkenylcarbonate may be brought into contact with the  
7 (co)polymer in various ways, depending upon the particular object of  
8 the modification process. For example, if surface modification of a  
9 three dimensional polymeric object is desired, the t-alkylperoxy  
10 alkenylcarbonate may simply be applied to the surface of the material  
11 to be modified. Alternatively, it is often desirable to distribute  
12 functional groups homogeneously throughout the (co)polymeric matrix.  
13 In this instance, the t-alkylperoxy alkenylcarbonate may be mixed with  
14 the material to be modified, which material may be in the molten  
15 state, in the form of a solution, or, in the case of an elastomer, in  
16 a plastic state. To accomplish homogeneous mixing of the material to  
17 be modified and the t-alkylperoxy alkenylcarbonate, most conventional  
18 mixing apparatus may be used. Typical mixing apparatus includes  
19 kneaders, internal mixers and (mixing) extruding equipment. Should  
20 mixing be a problem for a particular material because of its high  
21 melting point, for example, the (co)polymer can first be provided with  
22 functional groups on its surface while in the solid state and  
23 subsequently melted and mixed to distribute the functional groups  
24 throughout the material.

25 Alternatively, the (co)polymer may be first dissolved and the reaction  
26 with the present t-alkylperoxy alkenylcarbonates can then be carried  
27 out in solution.

28 An important practical aspect of the present invention is that the  
29 moment the t-alkylperoxy alkenylcarbonate and the (co)polymer are  
30 brought into contact with each other and also the moment that the t-  
31 alkylperoxy alkenylcarbonate is to react with the (co)polymer can be  
32 chosen independently of the other usual polymer processing steps,

including the introduction of additives, shaping, etc. For instance, the modification may be done before other additives are introduced into the polymer or after the introduction of other additives. More importantly, it is possible to accomplish the present polymer 5 modification during a polymer shaping step such as extrusion, compression moulding, blow moulding or injection moulding. The sole restriction applies to polymers which are to be cross-linked. In that case the t-alkylperoxy alkenylcarbonate should be contacted with the (co)polymer prior to cross-linking.

10 Examples of suitable (co)polymers which according to the present invention can be modified by means of epoxide or other types of functional groups such as carbonate groups, for example, are saturated (co)polymers such as polyethylene, e.g. LLDPE, MDPE, LDPE, and HDPE, 15 polypropylene, both isotactic and atactic, polyphenylene ether, ethylene/vinyl acetate copolymer, ethylene/ethylacrylate copolymer, ethylene/methylmethacrylate copolymer, ethylene/methacrylate copolymer, chlorinated polyethylene, fluor rubber, silicone rubber, polyurethane, polysulphide, polyacrylate rubber, ethylene/propylene 20 copolymer, pho phenylene oxides, nylon, polyesters such as polyethylene terephthalate and polybutylene terephthalate, polycarbonates, copolyetheresters, poly(butene-1), poly(butene-2), poly(isobutene), poly(methylpentene), polyvinyl chloride/acrylonitrile 25 graft copolymer, and combinations thereof. Unsaturated (co)polymers may also be modified by the unsaturated tertiary alkyl peroxy alkenyl carbonate of the present invention. Suitable unsaturated (co)polymers include polybutadiene, polyisoprene, poly(cyclopentadiene), poly(methylcyclopentadiene), partly dehydrochlorinated polyvinyl chloride, butadiene/styrene copolymer, acrylonitrile/butadiene/styrene 30 terpolymer, ethylene/propylene/dienemonomer terpolymer, isoprene/styrene copolymer, isoprene/isobutylene copolymer, isoprene/styrene/acrylonitrile terpolymer, polychloroprene, butadiene/acrylonitrile copolymer, natural rubber, and combinations thereof. Also, combinations of saturated and unsaturated polymers can

be modified in accordance with the present invention. In general, any (co)polymer comprising abstractable hydrogen atoms can be modified by the present process.

5 It has been found that when certain (co)polymers are contacted with the present peroxy alkenylcarbonates, some degradation of the polymer chains may occur. This degradation may affect the mechanical properties of the modified (co)polymer. Those polymers which are prone to formation of tertiary carbon radicals under the conditions of free  
10 radical reactions tend to undergo degradation. For instance, polymers which tend to degrade include polyisobutylene, poly( $\alpha$ -methyl)-styrene, polymethacrylates, polymethacrylamide, polyvinylidene chloride, polypropylene and particularly isotactic polypropylene, and polyvinyl alcohol. According to a preferred embodiment of the present invention, the modification process is conducted in the presence of a  
15 coagent in order to reduce or prevent the negative effects of polymer degradation or enhance the degree of modification of the (co)polymer.

20 A coagent is generally understood to be a polyfunctional reactive additive such as a polyunsaturated compound which will react rapidly with polymer radicals, will overcome steric hindrance effects and will minimize undesirable side reactions. Further information about coagents (which are sometimes called coactivators) is set forth in  
25 Rubber Chemistry and Technology, Vol. 61, pp. 238-254 and W. Hofmann, Progress in Rubber and Plastics Technology, Vol. 1, No. 2, March 1985, pp. 18-50, the disclosures of which are hereby incorporated by reference. In relation to the present invention the term "coagent" has the same meaning as given in these publications.

30 A wide variety of useful coagents are commercially available including di- and triallyl compounds, di-and tri(meth)acrylate compounds, bismaleimide compounds, divinyl benzene, vinyl toluene, vinyl pyridine, parachinone dioxime, 1,2-cis-polybutadiene and their derivatives. Furthermore, other useful coagents also include

oligomers of 1,3-diisopropenyl benzene, 1,4-diisopropenyl benzene, and 1,3,5-triisopropenyl benzene.

5 The incorporation of an effective amount of one or more of these coagents into the (co)polymer prior to or during the reaction with the present peroxy alkenylcarbonates will tend to reduce or prevent the degradation of the modified materials and thereby maintain the mechanical properties at the same level or better. Surprisingly, in 10 some cases the coagent may result in improved mechanical properties such as an enhanced adhesion strength in modified (co)polymers of a polar nature. This enhancement may be attributable to a greater degree of functional group introduction into the (co)polymer resulting from the presence of a coagent.

15 It may be preferable to modify polymers less liable to undergo degradation in the presence of coagents due to the greater amount of functional groups which can be introduced into the modified (co)polymer with the same quantity of peroxy alkenylcarbonate, in this manner. Such polymers, which are typically those that are 20 cross-linked when contacted with peroxides, include polyethylene, atactic polypropylene, polystyrene, polyacrylates, polyacrylamides, polyvinylchloride, polyamides, aliphatic polyesters, polyvinylpyrrolidone, unsaturated rubbers, polysiloxanes, ethylene/propylene rubbers, ethylene/propylene/diene rubbers and their 25 copolymers.

As a result of the present invention, the extremely useful physical and chemical properties resulting from the presence of epoxide, cyclic carbonate and/or ketone groups on the (co)polymers, can now be 30 obtained with an extremely large group of (co)polymers. The introduction of carbonate functionalities onto polymers is particularly useful for producing polyhydroxy or other types of polyurethanes without employing isocyanates such as is described in U.S. patent no. 3,084,140 and "Polyurethane Elastomers Obtained

Without the Use of Diisocyanates," Rappoport, L.Ya. et al., International Polymer Science and Technology, 8, No. 1, 1981, the disclosures of which are hereby incorporated by reference. In addition, further uses of cyclic carbonate-containing polymers are 5 detailed in U.S. patent 2,935,494, the disclosure of which is also hereby incorporated by reference.

10 The most preferred (co)polymers for modification by the compounds of the present invention are polyethylene, polypropylene, ethylene/propylene copolymer, ethylene/vinyl acetate copolymer, and ethylene/propylene/dienemonomer terpolymer.

15 The peroxy alkenylcarbonate of the present invention is generally used in an amount of 0.01 to 15% by weight, preferably 0.1 to 10% by weight, and most preferably 1.0 to 5.0% by weight, calculated on the basis of the weight of the (co)polymer. Mixtures of the peroxy alkenylcarbonates according to the invention may also be employed. In addition, in certain situations it may be advantageous to use an auxiliary free radical generator which has a decomposition temperature 20 lower than that of the peroxy alkenylcarbonate.

25 The (co)polymers modified in accordance with the present invention are useful for their standard applications although particular useful properties can be improved by the process of the present invention. In particular, due to the increased adhesion provided by the modification process, these modified (co)polymers are well suited for the fabrication of shaped objects. Further, these (co)polymers can be used in blends with other modified (co)polymers or with unmodified (co)polymers. For example, modified ethylene/propylene rubbers may be 30 blended with unmodified nylon to significantly improve the impact strength of the nylon composition.

The modification process itself, is generally carried out at temperatures in the range of 50°C to 250°C., and preferably from 100°C

to 200°C, care being taken that the duration of the modification reaction under the given conditions is at least several half-life periods of the peroxy alkenylcarbonate.

5 As mentioned above, the (co)polymer may also contain the usual polymer additives. As examples of such additives may be mentioned: stabilizers such as inhibitors of oxidative, thermal or ultraviolet degradation, lubricants, extender oils, pH controlling substances such as calcium carbonate, release agents, colorants, reinforcing or non-reinforcing fillers such as silica, clay, chalk, carbon black and fibrous materials, nucleating agents, plasticizers, accelerators, and cross-linking agents such as peroxides and sulfur. These additives may be employed in the usual amounts.

10 15 The invention is further described in the following examples.

Example 1

Preparation of t-Butylperoxy Allyl Carbonate

20 To a stirred mixture of 38.0 g. of water, 0.60 moles of t-butyl hydroperoxide (70% w/w) and 0.50 moles of allylchloroformate (98% w/w) were added over a period of 55 minutes. Then, 0.62 moles of an aqueous potassium hydroxide solution (45% w/w) was added with stirring at a temperature of 5-10°C and stirring was continued for an additional 45 minutes at 5-10°C. Thereafter, 60 g. of water was added to the reaction mixture at 10°C and the organic layer was separated and subsequently washed with 40 g. of an aqueous solution of NaOH (12.5% w/w) over a period of 5 minutes at 10°C; a mixture of 50 g. of water, 8 g. of NaAc/HAc buffer and 10 g. of Na<sub>2</sub>SO<sub>3</sub> solution over 15 minutes at 10°C; and a mixture of 54 g. of an aqueous solution of NaCl (25% w/w) and 6 g. of an aqueous solution of NaHCO<sub>3</sub> (6% w/w) over 15 minutes at 10°C. After drying the organic layer with a mixture of sodium sulfate and magnesium sulfate, 70.3 g. of a colorless liquid

was obtained having a peroxide content of 97.5% corresponding to a yield of 78.7%. The structure of the product was confirmed by NMR and IR spectroscopic analysis.

5      Example 2

Preparation of 2,5-bis(peroxyallylcarbonate) 2,5-Dimethyl Hexane

- To a stirred mixture of 115 ml of diethyl ether, 0.57 mol pyridine and 0.226 mole of 2,5-dimethyl-2,5-dihydroperoxyhexane (98% w/w) was added 0.534 mole of allylchloroformate (98% w/w) over a period of 55 minutes at 5-10°C. Stirring was continued for another period of 315 minutes at 5-10°C. Thereafter 145 g of water was added to the reaction mixture at 10°C. The organic layer was separated and subsequently washed with 84 g of HCl-1N, 5 minutes 5-10°C; 140 g of water, 5 minutes 5-10°C; four times with 50 g of an aqueous solution of KOH (2.5% w/w), 5 minutes 10°C; and 75 g of an aqueous solution of NaCl (2.5% w/w), 5 minutes 10°C.
- After drying the organic layer with  $MgSO_4 \cdot 2H_2O$ , the solvent was removed under reduced pressure 0.8 mbar at 10°C. A viscous liquid was obtained, peroxide content 90.0% corresponding to a yield of 69%.

The structure of the product was confirmed by NMR and IR spectroscopic analysis.

25

Example 3

Preparation of t-Butylperoxy Isopropenylcarbonate

- To a stirred mixture of 237 g. of n-pentane, 0.45 mole of pyridine and 0.40 mole of t-butylhydroperoxide (68% w/w in pentane) was added 0.396 mole of isopropenyl chloroformate (99% w/w) over a period of 35 minutes at 0°C. Stirring was continued for an additional period of 70 minutes at 0-5°C. Thereafter, 100 g. of water was added to the

reaction mixture at 0-5°C. The organic layer was then separated and subsequently washed with 100 g. of water over a period of 5 minutes at 0-5°C, 80 g. of 1 Normal HCl over a period of 5 minutes at 0-5°C twice, 85 g. of an aqueous solution of NaHCO<sub>3</sub> (2% w/w) over 5 minutes at 0-5°C twice, and 150 g. of an aqueous solution of NaCl (25% w/w) over 5 minutes at 0-5°C. After drying the organic layer with a mixture of Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>, the solvent was removed under a reduced pressure of 0.8 mbar at 10°C. 61 g. of a colorless liquid was obtained having a peroxide content of 89.7% corresponding to a yield of 79.3%. The structure of the product was confirmed by NMR and IR spectroscopic analysis.

#### Example 4

##### 15 Modification of Low Density Polyethylene

On a two-roll mill (225x110 mm.) at 110°C polyethylene in powder form (Lacqtene 1070 MN 040) is mixed with peroxy alkenylcarbonate. A Haake Rheocord System 40 fitted with an electrically heated roller mixer chamber type Rheomix 600 is employed to carry out the modification reaction. The mill is operated at 30 rpm (friction 3:2), a ram pressure of 60 kPa, and the reaction is carried out over a period of one hour. A modified low density polyethylene polymer is obtained. The amount of peroxy alkenylcarbonate, polymer, the reaction temperatures, the torque analysis and the physical properties of the modified polyethylene are listed in Table 1. The Fourier Transform Infrared (FTIR) spectrum for this modified polyethylene confirms the presence of cyclic carbonate functionalities in the polymers.

30 A sample of each modified polymer was compressed into a plate 1 mm thick over a period of 15 minutes, and at a temperature of 160°C. Subsequently, the peel strength of a bi-component lacquer and the lap shear strength using an epoxy resin were measured.

The 180° peel strength was determined according to ASTM-D 429-81 using a Zwick® tensile tester 1474 at 25 mm/min. Besides indicating the nature of the failure, the peel strength is reported by this method as (average peel force)/(diameter of test pieces).

5

The lap shear strength was measured using an epoxy resin of the following composition: 10 g. of bisphenol A/F epoxy resins (Epikote® DX 235, ex. Shell), 6 g. of polyaminoamide (Epilink® 177, ex. Akzo Chemicals) and 0.08 g. of silan® A 174 (ex. Union Carbide). A thin film of resin was applied to the adhesion surface area (20x15 mm) of a modified polymer plate (40x20x1 mm). Another modified polymer plate was placed on the adhesion surface area and the two parts were firmly clamped together to avoid occlusion of air. This composition was kept in a stove for 72 hours at 30°C.

10

The lap shear strength was determined on a Zwick® tensile tester 1474 by measuring the force (kg/cm<sup>2</sup>) needed to separate the plates from each other at a speed of 25 mm/min. If the adhesion fails by shifting apart of the two pieces of polymer, the measured force is a measure for adhesion of the epoxy resin. If the polymer breaks before the adhesion fails the force at which the adhesion will fail is not measurable but it will be at least higher than the force required for polymer breakage.

15

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25

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Table 1

	Reference Standard	t-butyldperoxy allyl carbonate	t-pentenylperoxy allyl carbonate
Amount of Lacqte 1070 MN040(g)	46.00	44.41	44.20
Amount of Modifying additive(g)	--	1.59	1.80
<u>Torque analysis</u>			
M <sub>min</sub> (Nm)	12.5	13.2	13.2
time till M <sub>min</sub> (min)	60	7.6	6.0
ΔM (Nm)	--	27.9	0.8
time till M <sub>max</sub> (min)	--	50	10
M <sub>60</sub> : torque after 60 min (Nm)	12.5	40	12.5
<u>Temperature analysis</u>			
temp. at M <sub>min</sub> (°C)	120	119	118
temp. at M <sub>max</sub> (°C)	120	148	121
max. temp. reached = T <sub>max</sub> (°C)	120	149	122
time till T <sub>max</sub> (min)	19.4	60.5	142
temp. end reaction (°C)	120	148	122
<u>Physical Properties</u>			
Adhesion-PUR lacquer(10 <sup>-2</sup> N/mm)	8	10	8
Maximum adhesion value(10x <sup>-2</sup> N/mm)	9.8	13.5	10.3
Lap Shear Strength (MPax10 <sup>-2</sup> )	23	28	33
Maximum lap shear value(MPax10 <sup>-2</sup> )	23	38	37

Example 5Modification of Polypropylene

5 Polypropylene (Hostalen PPU 0810 P) is mixed with peroxy alkenylcarbonate and a coagent. A Haake Rheocord System 40 fitted with an electrically heated roller mixer chamber type Rheomix 600 is employed to carry out the modification reaction. The mill is operated at 30 rpm (friction 3:2) and a ram pressure of 60 kPa, and the 10 reaction is carried out over a period of fifteen minutes. A modified polypropylene polymer is obtained. The amount of peroxy alkenylcarbonate, polymer, coagent, the reaction temperatures, the torque analysis and the physical properties of the modified polypropylene are listed in Table 2. The FTIR spectrum for 15 polypropylene modified with t-butyl peroxy allyl carbonate confirms the presence of cyclic carbonate functionalities in the modified polymer. The FTIR spectrum for polypropylene modified with t-butyl peroxy isopropenyl carbonate confirms the presence of ketone functionalities in the modified polymer.

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Table 2

Reference Standard	t-butylperoxy allyl carbonate	t-butylperoxy isopropenylcarbonate	t-pentenylperoxy allyl carbonate
Amount of Hostalen PPU0810(g)	44.88	43.36	43.24
Amount of Modifying additive(g)	--	1.56	1.68
Amount of Coagent (g.)	1.12	1.08	1.08
<b>Torque analysis</b>			
M <sub>min</sub> (Nm)	0.187	0.331	0.165
time till M <sub>min</sub> (min)	15	1.5	15
ΔM (Nm)	0	0.135	0
time till M <sub>max</sub> (min)	--	2.5	--
M <sub>15</sub> : torque after 60 min (Nm)	0.187	0.227	0.165
<b>Temperature analysis</b>			
temp. at M <sub>min</sub> (°C)	178	160	177
temp. at M <sub>max</sub> (°C)	--	165	--
max. temp. reached = T <sub>max</sub> (°C)	178	178	179
time till T <sub>max</sub> (min)	12.0	12.0	5.0
temp. end reaction (°C)	178	178	177
<b>Physical Properties</b>			
Adhesion-PUR lacquer (10 <sup>-2</sup> xN/mm)	8	15	9
Maximum adhesion value (10 <sup>-2</sup> xN/mm)	9.1	20	11
Lap Shear Strength (MPax10 <sup>-2</sup> )	23	> 95.6	> 101.2
Maximum lap shear value (MPax10 <sup>-2</sup> )	23	101.7	116.5
			125.0

Example 6Modification of Polyethylene With a Diallyl Peroxy Carbonate

- 5 Polyethylene in powder form (Lacqtene 1070 MN 040) is mixed with diallyl peroxy carbonate. A Haake Rheocord System 40 fitted with an electrically heated roller mixer chamber type Rheomix 600 is employed to carry out the modification reaction. The mill is operated at 30 rpm (friction 3:2), a ram pressure of 60 kPa, and the reaction is carried out over a period of one hour. A modified low density polyethylene polymer is obtained.

- 10
- 15 Modification of Polyphenylene Ether with t-Butyl Peroxy Allyl Carbonate

- 20 Polyphenylene ether (PPE), Noryl 800 in powder form (ex. General Electric Plastics) is modified with 20 meq./100g. PPE of t-butyl peroxy allyl carbonate in a roto vapor apparatus at 150°C over a period of 60 minutes.

- 25 The Fourier Transform Infrared (FTIR) Spectrum for the modified PPE demonstrates that the polymer contains cyclic carbonate functionalities. A sample of unmodified PPE shows no cyclic carbonate functionalities when subjected to FTIR analysis.

- 30 Blends of Modified PPE and Polyamid-6

The modified PPE from example 7 is blended with polyamid-6 (PA-6) (Akulon M138 ex. Akzo), in a weight ratio of modified PPE to PA-6 of 55/45. The blending is carried out in a Haake Rheomix 600 with roller

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sensors at 80 rpm, a set temperature of 260°C over a 10 minute period. The data from a torque analysis are presented in Table 3 for a standard blend of unmodified PPE with PA-6 and a blend of the modified PPE with PA-6 made in accordance with this example.

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The mechanical properties of the blends were determined on 200x120x1 mm compression molded sheets pressed at 260°C for 4 minutes without pressure, 1 minutes at 50 KN and 1 minute at 150 KN. The resultant properties were measured on a Zwick 1475 tensile tester according to 10 DIN 53504 and are also given in Table 3.

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Table 3  
 Standard PPE/PA-6      Modified PPE/PA-6

	Akulon M138 (PA-6)	45	45
5	Modified PPE	0	55
	PPE	55	0

Torque analyses:

10	Mmin	Nm	7.86	30.88
	time till Mmin	min	10.00	1.00
	delta M	Nm	0.00	21.08
	time till Mmax	min	-	1.30
	M10	Nm	7.86	14.32

Temperature analyses:

15	temp. at Mmin	°C	274	233
	temp. at Mmax	°C	274	246
	max. temp. reaches=Tmax	°C	275	284
	time till Tmax	min	7.00	7.30
	temp. end reaction	°C	274	284

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Mechanical Properties:

	Tensile Strength	MPa	35.89	48.45
	Elongation at Fmax	%	5.54	8.20
	Rupture Strength	MPa	35.90	47.00
25	Elongation at Rupture	%	5.54	9.26
	Youngs Modulus	MPa	1261.10	1946.19

30 As can be seen from the data presented in table 3, the modified PPE/PA-6 blends exhibit a higher torque, higher tensile strength, better elongation at rupture and a greater Young's modulus than the same blend using unmodified PPE.

Example 9Modification of High Density Powdered Polyethylene with t-Butyl Peroxy Allyl Carbonate

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High density polyethylene (HDPE), (Marlex 56020 in powder form, ex. Phillips Pet. Chem.), is modified with 20 meq./100 g. HDPE of t-butyl peroxy allyl carbonate in a roto vapor apparatus at 150°C over a period of 60 minutes. The FTIR spectrum for the modified HDPE demonstrates that the modified HDPE contains cyclic carbonates. The FTIR spectrum for unmodified HDPE shows no absorption band at the same frequency. This modified HDPE is useful in polymer blends or as a filler material for other polymers.

15

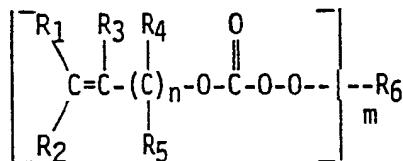
The foregoing examples show that polypropylene, polyphenylene ether and both high and low density polyethylene, when modified by the process of the present invention, exhibit improved physical properties. The ability to improve these physical properties by employing the simple and inexpensive process of the present invention provides a wide range of possibilities for improving the suitability of polymeric materials for their present applications as well as adapting these polymeric materials to new and different applications.

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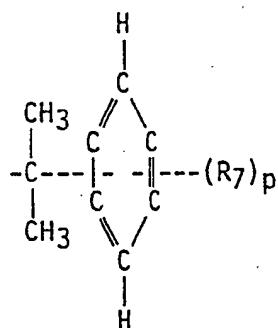
The foregoing description and examples of the invention were presented for the purpose of illustration and description only and are not to be construed as limiting the invention in any way. Accordingly, the scope of the invention is to be defined by the claims appended hereto.

What is claimed is:

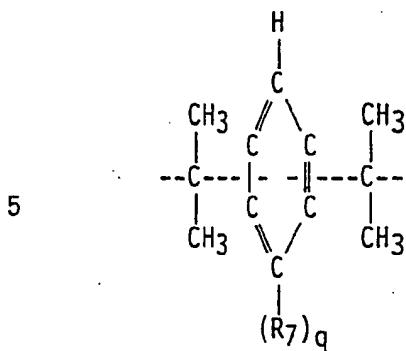
1. A process for the preparation of a modified (co)polymer by using an organic peroxide, said process comprising the step of contacting a peroxide of the formula:



10 wherein  $R_1$ ,  $R_2$ ,  $R_4$ , and  $R_5$  may be the same or different and represent H or  $C_{1-4}$  alkyl groups;  $n = 0$  or 1;  $m = 1$ , 2, or 3;  $R_3 = H$ ,  $C_{1-4}$  alkyl or an electron withdrawing group; and when  $m=1$ ,  $R_6 =$  a tertiary alkyl group optionally substituted with a hydroxyl group and containing 4-18 carbon atoms, *p*-menth-8-yl or a group of the general formula:



25 wherein  $p = 0$ , 1 or 2 and  $R_7$  is an isopropenyl group, a 2-hydroxyisopropyl group, or an isopropyl group; when  $m = 2$ ,  $R_6 =$  an alkylene group having 8-12 carbon atoms and a tertiary structure at both ends thereof, an alkynylene group having 8-12 carbon atoms and a tertiary structure at both ends thereof, or a group of the general formula:



10 wherein  $q = 0$  or  $1$  and  $R_7$  has the above-indicated meaning; and when  $m = 3$ ,  $R_6 = 1,2,4-triisopropylbenzene- $\alpha, \alpha', \alpha''$ -triyl or  $1,3,5$ -triisopropylbenzene- $\alpha, \alpha', \alpha''$ -triyl; with a (co)polymer whereby the peroxide is decomposed and the (co)polymer is modified.$

- 15 2. A process according to claim 1 characterized in that  $R_1$ ,  $R_2$  and  $R_3$  are selected from the group consisting of hydrogen and methyl.
3. A process according to claim 1 or 2, characterized in that  $m=2$ .
- 20 4. A process according to claim 1, characterized in that the peroxide is selected from the group consisting of t-butylperoxy allylcarbonate, t-pentenylperoxy allylcarbonate, t-butylperoxy isopropenylcarbonate, t-pentenylperoxy allylcarbonate, 2,5,-bis(peroxyallylcarbonate) 2,5-dimethyl hexane,
- 25 t-pentenylperoxy 4-propyl-4-heptene carbonate, t-octylperoxy 3-butyl-3-hexene carbonate and t-nonylperoxy 2-methyl-2-pentene carbonate.
- 30 5. A process according to any one of claims 1-4, characterized in that the amount of peroxide that is contacted with the (co)polymer is 0.01 to 15% by weight of the (co)polymer, the reaction temperature is from 50-250°C, and the duration of the modification step is at least five half-life periods of the peroxide.

6. A process according to claim 5, characterized in that the added amount of peroxide is 0.1 to 10% by weight of the (co)polymer and the reaction temperature is from 100-200°C.
- 5 7. A process according to any one of claims 1-6, further characterized in that the peroxide is contacted with the (co)polymer in the presence of a coagent.
- 10 8. A process according to claim 7, wherein the coagent is selected from the group consisting of di- and triallyl compounds, di- and tri-(meth)acrylate compounds, bismaleimide compounds, divinyl compounds, polyalkenylbenzenes and their polymers, vinyl toluene, vinyl pyridine, parachinone dioxime, polybutadiene and their derivatives.
- 15 9. A process according to one of claims 1-8, characterized in that the (co)polymer is selected from the group consisting of polyethylene, polypropylene, polyphenylene ether, ethylene/propylene copolymer, ethylene/vinylacetate copolymer, ethylene/propylene/dienemonomer terpolymer, 2,6-dimethylpolyphenyleneoxide, and mixtures thereof.
- 20 10. A process according to any one of claims 1-9, characterized in that the (co)polymer is degraded during the modification step.
- 25 11. A process according to any one of claims 1-9, characterized in that the (co)polymer is cross-linked during the modification step.
- 30 12. A shaped object manufactured using a (co)polymer prepared by the process according to any one of claims 1-11.
13. A shaped object manufactured using two or more (co)polymers, of which at least one is a (co)polymer prepared by the process according to any one of claims 1-11.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/EP 90/01045

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>5</sup> C 08 F 8/50

## II. FIELDS SEARCHED

Classification System	Minimum Documentation Searched *	
		Classification Symbols
IPC <sup>5</sup>		C 08 F, C 08 K
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	GB, A, 2081282 (NIPPON OIL AND FATS) 17 February 1982 see claim 1 (cited in the application)	1
A	EP, A, 0208353 (AKZO) 14 January 1987 see claims 1-5	1
A	EP, A, 0273990 (AKZO) 13 July 1988 see claims 1-6 (cited in the application)	1
A	EP, A, 0273274 (LUPEROX) 6 July 1988 see claims 1-11; page 5	1

\* Special categories of cited documents: <sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
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## IV. CERTIFICATION

Date of the Actual Completion of the International Search

15th October 1990

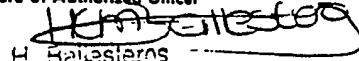
Date of Mailing of this International Search Report

09.11.90

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Signature of Authorized Officer

  
H. Balesterns

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

EP 9001045  
SA 38451

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 30/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2081282	17-02-82	JP-A, B, C57023615 FR-A, B 2486951 NL-A- 8103414 US-A- 4366290	06-02-82 22-01-82 16-02-82 28-12-82
EP-A- 0208353	14-01-87	CA-A- 1271585 JP-A- 62001733 US-A- 4833209 US-A- 4774293	10-07-90 07-01-87 23-05-89 27-09-88
EP-A- 0273990	13-07-88	None	
EP-A- 0273274	06-07-88	DE-A- 3642266	23-04-87

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